

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> C09K 15/06, A23L 3/3436, C07C 49/786, 45/46, B32B 27/18, B65D 81/26, 51/24, C08K 5/00	<b>A1</b>	<b>(11) International Publication Number:</b> WO 98/51758  <b>(43) International Publication Date:</b> 19 November 1998 (19.11.98)
<b>(21) International Application Number:</b> PCT/US98/07734  <b>(22) International Filing Date:</b> 16 April 1998 (16.04.98)  <b>(30) Priority Data:</b> 08/857,325 16 May 1997 (16.05.97) US  <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US).  <b>(72) Inventors:</b> KATSUMOTO, Kiyoshi; 2615 Brooks Avenue, El Cerrito, CA 94530 (US). CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US). GOODRICH, Joseph, L.; 3545 Wilkinson Lane, Lafayette, CA 94549 (US). SPEER, Drew, Ve; 6229 Slender Sky, Columbia, MD 21044 (US).  <b>(74) Agents:</b> HAYMOND, W., Bradley et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTOINITIATORS AND OXYGEN SCAVENGING COMPOSITIONS  <b>(57) Abstract</b>  An oxygen scavenging composition or system is provided comprising an oxygen scavenging material, a photoinitiator, and at least one catalyst effective in catalyzing an oxygen scavenging reaction, wherein the photoinitiator comprises a benzophenone derivative containing at least two benzophenone moieties. A film, a multi-phase composition, a multi-layer composition, a multi-layer film, an article comprising the oxygen scavenging composition, a method for preparing the oxygen scavenging composition, and a method for scavenging oxygen are also provided. Non-extractable benzophenone derivative photoinitiators and methods for preparing same are also provided.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1       PHOTOINITIATORS AND OXYGEN SCAVENGING COMPOSITIONS

2                               FIELD OF THE INVENTION

3       The present invention relates to photoinitiators, methods for preparing and using  
4       same, oxygen scavenging compositions, articles made from same and methods  
5       of scavenging oxygen.

6                               BACKGROUND OF THE INVENTION

7       The term "oxygen scavenging" means to absorb, deplete, or react with oxygen  
8       from a given environment.

9       Oxygen scavenging materials have been developed partly in response to the  
10      food industry's goal of having longer shelf-life for packaged food. One method  
11      which is currently being employed involves the use of "active packaging" where  
12      the package is modified in some way so as to control the exposure of the  
13      product to oxygen. Such "active packaging" can include sachets containing  
14      iron-based compositions such as AGELESS™ which scavenges oxygen within  
15      the package through an oxidation reaction. However, such an arrangement is  
16      not advantageous for a variety of reasons including the accidental ingestion of  
17      the sachets or the oxygen scavenging material present therein.

18     Other techniques involve incorporating an oxygen scavenger into the package  
19     structure itself. In such an arrangement, oxygen scavenging materials constitute  
20     at least a portion of the package, and these materials remove oxygen from the  
21     enclosed package volume which surrounds the product or which may leak into  
22     the package, thereby, in the case of food products, inhibiting spoilage and  
23     prolonging freshness.

1 Oxygen scavenging materials include low molecular-weight oligomers that are  
2 typically incorporated into polymers or can be oxidizable organic polymers. Such  
3 oxygen scavenging materials are typically employed with a suitable catalyst, e.g.,  
4 an organic or inorganic salt of a transition metal catalyst.

5 The onset of useful oxygen scavenging activity may not occur for as long as 30  
6 days. In order to shorten the induction period and to initiate oxygen scavenging,  
7 photoinitiators can be employed in conjunction with actinic radiation. Many of  
8 these photoinitiators and resulting by-products are extractable and can leach into  
9 the headspace surrounding the packaged product or even enter the product  
10 itself. Such leaching can produce foul odors or unpleasant taste or can be  
11 otherwise undesirable.

12 SUMMARY OF THE INVENTION

13 It is an object of the present invention to provide a composition effective for  
14 oxygen scavenging under typical storage conditions.

15 It is another object of the present invention to provide a composition which is  
16 effective for oxygen scavenging at low temperatures.

17 It is another object of the present invention to provide an oxygen scavenging  
18 composition which produces reduced levels of extractable compounds.

19 It is another object of the present invention to provide an oxygen scavenging  
20 composition which has a short initiation period upon activation.

21 It is another object of the present invention to provide an oxygen scavenging  
22 composition which exhibits improved shelf life prior to activation.

- 1 It is another object of the present invention to provide a film or a multi-layer film
- 2 capable of scavenging oxygen.
- 3 It is another object of the present invention to provide an article, package or
- 4 container suitable for oxygen scavenging.
- 5 It is another object of the present invention to provide a method for preparing an
- 6 oxygen scavenging composition.
- 7 It is another object of the present invention to provide a method for scavenging
- 8 oxygen.
- 9 It is another object of the present invention to provide novel photoinitiators which
- 10 are effective initiators for oxygen scavenging.
- 11 It is another object of the present invention to provide novel photoinitiators which
- 12 are essentially non-leachable.
- 13 It is another object of the present invention to provide methods for preparing
- 14 novel photoinitiators.
- 15 According to the present invention, an oxygen scavenging composition or system
- 16 is provided comprising an oxygen scavenging material, a photoinitiator, and at
- 17 least one catalyst effective in catalyzing the oxygen scavenging reaction. The
- 18 photoinitiator comprises a benzophenone derivative containing at least two
- 19 benzophenone moieties. A film, a multi-phase composition, a multi-layer
- 20 composition, a multi-layer film, an article comprising the oxygen scavenging
- 21 composition, as well as a method for preparing the oxygen scavenging
- 22 compositions, and a method for scavenging oxygen are also provided.

1 According to other aspects of the present invention, non-extractable  
2 photoinitiators and methods for preparing same are provided.

3 BRIEF DESCRIPTION OF THE DRAWINGS

4 Figures 1, 2 and 3 are a graphic representation of the effectiveness of various  
5 photoinitiators.

6 DETAILED DESCRIPTION OF THE INVENTION

7 It has been found that benzophenone derivatives containing at least two  
8 benzophenone moieties act as effective photoinitiators to initiate oxygen  
9 scavenging activity in oxygen scavenging compositions and to provide a  
10 composition having a very low degree of extraction of the photoinitiators which  
11 may contaminate a packaged product. By benzophenone moiety is meant a  
12 substituted or unsubstituted benzophenone group. Suitable substituents are any  
13 substituent which does not interfere with the objects of the invention and include  
14 alkyl, aryl, alkoxy, phenoxy, and alicyclic groups containing from 1 to 24 carbon  
15 atoms or halides.

16 These derivatives are substantially non-extractable by most organic solvents at  
17 room temperature. By substantially non-extractable is meant that less than  
18 about 500 ppb photoinitiator are extracted through a 0.5 mil polyethylene film in  
19 ten days at room temperature from an oxygen scavenging composition  
20 containing 1000 ppm by weight photoinitiator when exposed to 10 g fatty food  
21 simulant per square inch of 1 mil film, preferably 250 ppb photoinitiator or less  
22 are extracted, more preferably 100 ppb photoinitiator or less are extracted, and  
23 most preferably 50 ppb photoinitiator or less are extracted.

1 Such benzophenone derivatives include dimers, trimers, tetramers, and  
2 oligomers of benzophenone-type photoinitiators derived from benzophenone and  
3 substituted benzophenones, as fully described herein below.

4 The substantially non-extractable photoinitiators are represented by the following  
5 formula:



7 Wherein each X is a bridging group selected from the group consisting of sulfur;  
8 oxygen; carbonyl;  $-\text{SiR}_2-$ , wherein each R is individually selected and is an alkyl  
9 group containing from 1 to 12 carbon atoms, an aryl group containing 6 to  
10 12 carbon atoms, or an alkoxy group containing from 1 to 12 carbon atoms;  
11  $-\text{NR}'-$ , wherein R' is an alkyl group containing 1 to 12 carbon atoms, aryl group  
12 containing 6 to 12 carbon atoms, or hydrogen; and an organic group containing  
13 from 1 to 50 carbon atoms, preferably from 1 to 40 carbon atoms. X can be a  
14 divalent group or can be a polyvalent group with 3 or more benzophenone  
15 moieties attached. Wherein m is 0 to 11.

16 The organic bridging group, when present, can be linear, branched, cyclic  
17 including fused or separate cyclic groups or an arylene group which can be fused  
18 or non-fused polyaryl groups. The organic bridging group can contain one or  
19 more heteroatoms such as oxygen, nitrogen, phosphorous, silicon or sulfur or  
20 combinations thereof. Oxygen can be present as an ether, ketone, ester, or  
21 alcohol.

22 Wherein each Y is a substituted or unsubstituted benzophenone group. Wherein  
23 each substituent, R'', when present, is individually selected from any substituent  
24 which does not substantially interfere with the objects of the invention and

- 1 include alkyl, aryl, alkoxy, phenoxy, or alicyclic groups containing from 1 to  
2 24 carbon atoms, or halides. Each benzophenone moiety can have up to  
3 9 substituents. Wherein n is 2-12.
- 4 Preferably, the combined molecular weight of the X and R" groups is at least  
5 about 30 g/mole. Appropriate choice of substituents can render the photoinitiator  
6 more compatible with the oxygen scavenging composition. Such substituents  
7 include alkyl and alkoxy for example.
- 8 Preferably, the oxygen scavenging composition consumes half of the available  
9 oxygen in a container containing 1 percent oxygen in less than 4 days at 25°C.  
10 More preferably, the oxygen scavenging composition consumes half of the  
11 available oxygen in a container containing 1 percent oxygen in less than 4 days  
12 at 4°C.
- 13 The photoinitiators include multiplets of ultraviolet (UV) initiators linked by cross  
14 conjugation so as to retain the UV absorption characteristics with enhanced UV  
15 absorptivity, i.e., higher extinction coefficient. The linkages within the dimers,  
16 trimers, tetramers, and oligomers can be flexible or rigid. The rigid type are  
17 preferred for lower extractability. However, a certain degree of flexibility is  
18 required to facilitate the melt blending to allow a molecular level distribution in  
19 the polymer films.
- 20 Typically, these compounds have a strong UV absorption at about 200-400 nm.  
21 Generally, the molecular weight will be greater than about 360 g/mole, preferably  
22 in the range of from about 360 g/mole to about 5000 g/mole, more preferably in  
23 the range of from 390 g/mole to 4000 g/mole.

1 The photoinitiators are substantially non-extractable by most organic solvents  
2 when incorporated into oxygen scavenging compositions. They provide efficient  
3 light absorption to trigger a photochemical induced oxidation. The photoinitiators  
4 are stable and do not fragment into extractable by-products. The photoinitiators  
5 are also large enough or rigid enough to be immobile and therefore cannot be  
6 leached into the packaged food or product. The photoinitiators do not sublime  
7 under normal processing and handling conditions. This assures an extended  
8 shelf life for the preactivated composition and a safe packaging material  
9 according to U.S. Food and Drug Administration standards.

10 Examples of non-extractable photoinitiators include dibenzoyl biphenyl,  
11 substituted dibenzoyl biphenyl, benzoylated terphenyl, substituted benzoylated  
12 terphenyl, tribenzoyl triphenylbenzene, substituted tribenzoyl triphenylbenzene,  
13 benzoylated styrene oligomer, and substituted benzoylated styrene oligomer.  
14 Benzoylated styrene oligomer is a mixture of compounds containing from 2 to  
15 12 repeating styrenic groups comprising dibenzoylated 1,1-diphenyl ethane,  
16 di-benzoylated 1,3 diphenyl propane, di-benzoylated 1-phenyl naphthalene,  
17 dibenzoylated styrene dimer, dibenzoylated styrene trimer and tribenzoylated  
18 styrene trimer.

19 Suitable substituents for the above compounds include any substituent which  
20 does not interfere substantially with the objects of the invention and include alkyl,  
21 aryl, alkoxy, phenoxy, and alicyclic groups containing from 1 to 24 carbon atoms  
22 or halides.

23 Typical examples of suitable alkyl groups include methyl, ethyl, propyl, isopropyl,  
24 butyl, t-butyl, pentyl, dodecyl, hexadecyl, octadecyl and the like. Specific  
25 examples of alkoxy groups include methoxy, ethoxy, propoxy, butoxy,

- 1 dodecyloxy and the like. Examples of alicyclic groups include cyclopentyl,  
2 cyclohexyl, cycloheptyl and the like. The hydrocarbon substituents can be  
3 saturated or can contain ethylenic unsaturation.
- 4 Examples of specific photoinitiators include 4,4'-bis(4,4'-dimethyldibenzoyl)  
5 biphenyl; 4,4'-bis(4,4'-diethyldibenzoyl) biphenyl; 4,4'-bis(2,2'-dimethyldibenzoyl)  
6 biphenyl; 4,4'-bis(2,2'-dimethoxydibenzoyl) biphenyl; 4,4'-bis(4-  
7 dodecyldibenzoyl) biphenyl; 4,4'-bis(2,2'-diacetyldibenzoyl) biphenyl;  
8 4,4'-bis(4,4'-dimethyldibenzoyl) diphenyl ether; 4,4'-bis(4,4'-diethyldibenzoyl)  
9 diphenyl ether; 4,4'-bis(2,2'-dimethyldibenzoyl) diphenyl ether;  
10 4,4'-bis(2,2'-dimethoxydibenzoyl) diphenyl ether; 4,4'-bis(4-dodecyldibenzoyl)  
11 diphenyl ether; 4,4'-bis(2,2'-diacetyldibenzoyl)diphenyl ether;  
12 4,4'-bis(4,4'-dimethyldibenzoyl)diphenyl sulfide; 4,4'-bis-  
13 diethyldibenzoyl)diphenyl sulfide; 4,4'-bis(2,2'-dimethyldibenzoyl)diphenyl sulfide;  
14 4,4'-bis(2,2'-dimethoxydibenzoyl) diphenyl sulfide; 4,4'-bis(4-dodecyldibenzoyl)  
15 diphenyl sulfide; 4,4'-bis(2,2'-diacetyldibenzoyl) diphenyl sulfide;  
16 4,4'-bis(4,4'-dimethyldibenzoyl) diphenyl amine; 4,4'-bis(4,4'-diethyldibenzoyl)  
17 diphenyl amine; 4,4'-bis(2,2'-dimethyldibenzoyl) diphenyl amine;  
18 4,4'-bis(2,2'-dimethoxydibenzoyl) diphenyl amine; 4,4'-bis(4-dodecyldibenzoyl)  
19 diphenyl amine; 4,4'-bis(2,2'-diacetyldibenzoyl) diphenyl amine;  
20 4,4'-bis(4,4'-dimethyldibenzoyl) diphenyl dimethyl silane;  
21 4,4'-bis(4,4'-diethyldibenzoyl) diphenyl dimethyl silane; 4,4'-bis(2,2'-  
22 dimethyldibenzoyl) diphenyl dimethylsilane; 4,4'-bis(2,2'-dimethoxydibenzoyl)  
23 diphenyl dimethyl silane; 4,4'-bis(4-dodecyldibenzoyl) diphenyl dimethyl silane;  
24 4,4'-bis(2,2'-diacetyldibenzoyl) diphenyl dimethyl silane;  
25 4,4'-bis(4,4'-dimethyldibenzoyl) benzophenone; 4,4'-bis(4,4'-diethyldibenzoyl)  
26 benzophenone; 4,4'-bis(4,4'-dipropyldibenzoyl) benzophenone;  
27 4,4'-bis(2,2'-dimethoxydibenzoyl) benzophenone; 4,4'-bis(4-dodecyldibenzoyl)

- 1 benzophenone; 4,4-bis(2,2'-diacetyldibenzoyl) benzophenone;  
2 4,4'-bis(4,4'-dimethyldibenzoyl) diphenyl methane; 4,4'-bis(4,4'-diethyldibenzoyl)  
3 diphenyl methane; 4,4'-bis(4,4'-dipropyldibenzoyl) diphenyl methane;  
4 4,4'-bis(2,2'-dimethoxydibenzoyl) diphenyl methane; 4,4-bis(4-dodecyldibenzoyl)  
5 diphenyl methane; 4,4'-bis(2,2'-diacetyldibenzoyl) diphenyl methane;  
6 4,4'-dibenzoyl-1,4-diphenoxy butane; 4,4'-dibenzoyl-1,2-diphenoxy ethane;  
7 4,4'-bis(4,4'-dimethyldibenzoyl)-1,4-diphenoxy butane; 4,4'-dibenzoyl-1,12-  
8 diphenoxy dodecane; tritoluoyl triphenyl benzene, tri(para-methoxybenzoyl)  
9 triphenyl benzene, dibenzoyl meta-terphenyl, ditoluoyl meta-terphenyl, ditoluoyl  
10 para-terphenyl, diethyldibenzoyl meta-terphenyl, dipropyldibenzoyl  
11 ortho-terphenyl, dibutyldibenzoyl para-terphenyl, dipentyldibenzoyl  
12 meta-terphenyl, dihexyldibenzoyl ortho-terphenyl, diheptyldibenzoyl  
13 para-terphenyl, dioctyldibenzoyl meta-terphenyl, dioctadecyl dibenzoyl  
14 ortho-terphenyl, and the like.
- 15 The photoinitiator is present in an amount sufficient to decrease the induction  
16 period after UV triggering. The amount of photoinitiator employed can vary  
17 broadly depending on the oxygen scavenging material employed, the  
18 wavelength, time of exposure and intensity of the radiation used, the type of  
19 photoinitiator, time of exposure and the amount of antioxidants employed, if any.
- 20 Generally, the photoinitiator will be present in an amount in the range of from  
21 about 0.001 weight percent to about 10 weight percent based on the total weight  
22 of the oxygen scavenging composition, preferably from 0.005 weight percent to  
23 5 weight percent, and more preferably from 0.01 weight percent to 1 weight  
24 percent.

1 An effective photoinitiator is one which provides the oxygen scavenging  
2 composition an induction period of one day or less. The photoinitiator should be  
3 effective at 25°C and preferably also effective at 4°C.

4 The photoinitiator can be introduced into the oxygen scavenging composition by  
5 any method known in the art such as coating techniques and extrusion  
6 compounding (including masterbatching). The photoinitiators can be introduced  
7 into polymers under conventional melt processing conditions to provide good  
8 mixing without plate-out on the machine.

9 The photoinitiator tribenzoyl triphenylbenzene can be prepared by reacting a  
10 benzoyl halide, such as benzoyl chloride, and a triphenylbenzene. The benzoyl  
11 halide and triphenylbenzene can contain additional substituents. Suitable  
12 substituents comprise any substituent which does not interfere substantially with  
13 the reaction and include alkyl, aryl, alkoxy, phenoxy, and alicyclic groups  
14 containing from 1 to 24 carbon atoms or halides.

15 Preferably, an aluminum- or boron-containing catalyst such as aluminum  
16 trichloride or boron trifluoride is employed.

17 Conditions for reacting the benzoyl chloride and triphenylbenzene can vary  
18 broadly. Generally, the reaction temperature is in the range of from about -20°C  
19 to about 150°C, preferably from about -10°C to about 120°C. The pressure is  
20 not critical and ambient pressure is suitable. Typically, the reaction would be  
21 conducted in a suitable diluent such as nitrobenzene, chlorobenzene,  
22 dichlorobenzene, dichloromethane, dichloroethane, trichloroethane, or carbon  
23 disulfide.

1 The photoinitiator benzoylated styrene oligomer can be prepared by reacting  
2 styrene trimers with a benzoyl halide, such as benzoyl chloride. Styrene trimers  
3 can be distilled from a polystyrene by-products stream. The benzoyl halide and  
4 styrene trimers can contain additional substituents. Suitable substituents  
5 comprise any substituent which does not interfere substantially with the reaction  
6 and include alkyl, aryl, alkoxy, phenoxy, and alicyclic groups containing from 1 to  
7 24 carbon atoms or halides.

8 Preferably, an aluminum- or boron-containing catalyst such as aluminum  
9 trichloride or boron trifluoride is employed.

10 The reaction produces a mixture of products including the major components  
11 di-benzoylated styrene trimer, tri-benzoylated styrene pentamer,  
12 tetra-benzoylated styrene pentamer, di-benzoylated styrene dimer, and minor  
13 components including benzoylated 1-phenyl naphthalene, benzoylated styrene  
14 dimer, di-benzoylated 1,3 di-phenyl propane, di-benzoylated 1-phenyl  
15 naphthalene, benzoylated 1,1-di-phenyl ethane, and benzoylated ethyl-benzene.

16 Conditions for reacting the benzoyl halide and styrene trimers can vary broadly.  
17 Generally, the reaction temperature is in the range of from about 0°C to about  
18 100°C. The pressure is not critical and ambient pressure is suitable.

19 The photoinitiator benzoylated terphenyl can be prepared by reacting a terphenyl  
20 and a benzoyl halide, such as benzoyl chloride. The terphenyl can be para-,  
21 meta- or ortho-terphenyl. The terphenyl and benzoyl halide can contain  
22 additional substituents. Suitable substituents comprise any substituent which  
23 does not interfere substantially with the reaction and include alkyl, aryl, alkoxy,  
24 phenoxy, and alicyclic groups containing from 1 to 24 carbon atoms or halides.

1 Generally, a catalyst such as aluminum chloride is employed. The reaction is  
2 generally conducted in a suitable solvent such as nitrobenzene, chlorobenzene,  
3 dichlorobenzene, dichloromethane, dichloroethane, trichloroethane, or carbon  
4 disulfide.

5 Conditions for reacting the terphenyl and benzoyl halide can vary broadly.  
6 Generally, the reaction temperature is in the range of from about 0°C to about  
7 100°C. The product comprising di-benzoylated terphenyl can be isolated by  
8 recrystallization from toluene.

9 The oxygen scavenging material can be any material known in the art to  
10 scavenge oxygen, providing that the material does not compete strongly for UV  
11 absorption in the critical region where the photoinitiator absorbs light. The  
12 oxygen scavenging material can be any organic compound or polymer which  
13 contains an oxidizable site. Preferred compounds include ethylenically  
14 unsaturated compounds and those containing benzylic, allylic and/or tertiary  
15 hydrogen. Examples of such organic compounds include squalene, dehydrated  
16 castor oil, polybutene or polypropylene.

17 Substituted oxidizable polymers include polymers and copolymers containing  
18 esters, carboxylic acids, aldehydes, ethers, ketones, alcohols, peroxides, and/or  
19 hydroperoxides. Preferably, the oxidizable polymers contain two or more  
20 ethylenically unsaturated sites per molecule, more preferably three or more  
21 ethylenically unsaturated sites per molecule.

22 Other oxidizable compounds suitable as oxygen scavenging materials include  
23 those described in U.S. Pat. Nos. 5,211,875 and 5,346,644 to Speer et al., which  
24 are hereby incorporated by reference in their entirety. Examples of oxidizable

1 compounds include polybutadiene, polyisoprene, styrene-butadiene block  
2 copolymers, polyterpenes, poly(meta-xylenedipamide) (also known as MXD6),  
3 polymers of fatty acids such as oleic, ricinoleic, dehydrated ricinoleic, and linoleic  
4 acids and esters of such acids, acrylates which can be prepared by  
5 transesterification of poly(ethylene-methyl acrylate) such as poly(ethylene-methyl  
6 acrylate-benzyl acrylate), poly(ethylene-methyl acrylate-tetrahydrofurfuryl  
7 acrylate), poly(ethylene-methyl acrylate-nopol acrylate) and mixtures thereof.  
8 Such transesterification processes are disclosed in U.S. Serial No. 08/475,918  
9 filed June 7, 1995, the disclosure of which is hereby incorporated by reference.  
10 Butadiene polymers and copolymers, such as styrene-butadiene-styrene block  
11 copolymer, are preferred for low temperature applications requiring  
12 transparency.

13 The polyterpenes such as poly(alpha-pinene), poly(dipentene),  
14 poly(beta-pinene), and poly(limonene) are especially effective oxygen scavenger  
15 materials and produce reduced amounts of migratory carboxylic acids,  
16 aldehydes and alkenes which can produce objectionable odors and tastes.

17 The oxygen scavenging material can be introduced into the oxygen scavenging  
18 system by a variety of techniques. The oxygen scavenging material can be  
19 formed into films which can be a separate layer in a multi-layer structure, coated  
20 or laminated onto a material such as aluminum foil or paper, formed into bottles  
21 or other rigid containers, or even incorporated into a material such as paper, for  
22 example, in flexible and rigid packaging. The oxygen scavenging material can  
23 also be in a localized area on a layer; for example, it may be in a patch that is  
24 laminated to another layer. The oxygen scavenging composition can contain a  
25 mixture of two or more oxidizable organic compounds.

1 The oxygen scavenging material is generally present in the oxygen scavenging  
2 composition in an amount sufficient to scavenge at least 0.1 cc O<sub>2</sub>/gram of  
3 oxygen scavenging composition/day at 25°C. Preferably, it is capable of  
4 scavenging at least about 0.5 cc O<sub>2</sub>, and more preferably at least about 1 cc  
5 O<sub>2</sub>/gram of oxygen scavenging composition/day at 25°C. For many applications,  
6 such as food and beverage storage, it is desirable to select an oxygen  
7 scavenging material which will effectively scavenge oxygen as indicated at a  
8 temperature of 4°C.

9 The amount of oxygen scavenging material employed in the oxygen scavenging  
10 composition can vary broadly depending on the desired characteristics of the  
11 final product. Generally, the oxygen scavenging material is present in an amount  
12 in the range of from about 1 weight percent to about 99 weight percent based on  
13 the total oxygen scavenging composition, preferably from about 5 weight percent  
14 to about 95 weight percent, and more preferably from 10 weight percent to  
15 90 weight percent.

16 The catalyst can be any catalyst known in the art which is effective in initiating  
17 the oxygen scavenging reaction. Typical catalysts include transition metal salts.  
18 Suitable catalysts are disclosed in U.S. Pat. Nos. 5,211,875 and 5,346,644 to  
19 Speer et al., the disclosures of which were previously incorporated by reference  
20 in their entirety. Suitable transition metal salts are those which contain  
21 manganese, iron, cobalt, nickel, copper, rhodium, and ruthenium, preferably iron,  
22 nickel copper, manganese or cobalt.

23 Cobalt compounds containing organic or inorganic anions are preferred.  
24 Suitable anions include chloride, acetate, stearate, caprylate, palmitate,  
25 2-ethylhexanoate, citrate, glycolate, benzoate, neodecanoate, naphthenate,

1   oleate, and linoleate. Organic anions are preferred and cobalt oleate, cobalt  
2   linoleate, cobalt neodecanoate, cobalt stearate and cobalt caprylate are  
3   especially preferred. It has been found that a composition comprising the  
4   combination of cobalt stearate and benzoylated styrene oligomer is especially  
5   effective at scavenging oxygen at low temperature and oxygen levels, e.g., 1%  
6   oxygen levels at 4°C.

7   The catalyst is present in an amount sufficient to catalyze the oxygen  
8   scavenging reaction. Generally, the catalyst will be present in an amount in the  
9   range of from about 10 parts per million by weight (ppm) to about 10,000 ppm by  
10   weight transition metal ion based on the total weight of the oxygen scavenging  
11   composition, preferably from 10 ppm to 5,000 ppm transition metal ion.

12   The catalyst can be introduced in any manner which does not react with and/or  
13   deactivate the catalyst. For example, the catalyst can be applied onto the  
14   oxygen scavenging material by any suitable means, e.g., coating techniques  
15   such as spray coating, extrusion compounding or lamination. Further, the  
16   catalyst may be included as part of a compounded master batch using a suitable  
17   carrier resin.

18   The oxygen scavenging composition can be activated by methods known in the  
19   art such as by actinic radiation, i.e., ultraviolet or visible light having a wave  
20   length in the range of from about 200 nm to about 750 nm, electron beam, or  
21   thermal triggering. Such methods are described in U.S. Pat. No. 5,211,875, the  
22   disclosure of which is hereby incorporated by reference. The composition is  
23   typically activated with at least 0.1 J/cm<sup>2</sup>, preferably in the range of from  
24   0.5 J/cm<sup>2</sup> to 200 J/cm<sup>2</sup> of UV radiation in the range of from 200 nm to 400 nm,  
25   preferably in the range of from 0.5 J/cm<sup>2</sup> to 100 J/cm<sup>2</sup>, and more preferably in the

1 range of from 0.5 J/cm<sup>2</sup> to 20 J/cm<sup>2</sup>. The composition can also be activated with  
2 an electron beam at a dosage of about 0.2 to 20 megarads, preferably about 1 to  
3 10 megarads. Other sources of radiation include ionizing radiation, such as  
4 gamma, x-rays or corona discharge. The radiation is preferably conducted in the  
5 presence of oxygen.

6 The duration of exposure depends on several factors including the amount and  
7 type of photoinitiator present, thickness of the layers to be exposed, amount of  
8 any antioxidant present, and the wavelength and intensity of the radiation  
9 source. The activation is conducted prior to using the layer or article. Exposure  
10 to a flat layer or article provides the most uniform radiation.

11 For many applications, the oxygen scavenging composition can contain a diluent  
12 polymer to provide desired characteristics. Suitable diluent polymers include  
13 polyethylene, polypropylene, poly(vinyl chloride), and ethylene copolymers such  
14 as ethylene-vinyl acetate, ethylene-alkyl acrylates, ethylene-acrylic acid,  
15 ethylene-acrylic acid ionomers, and mixtures thereof.

16 In another aspect of the invention, the oxygen scavenging composition  
17 comprises a first phase comprising the oxygen scavenging material and a  
18 second phase comprising the catalyst. Such compositions are disclosed in U.S.  
19 Serial No. 08/388,815 filed February 15, 1995, the disclosure of which is  
20 incorporated herein by reference. The first phase is essentially devoid of  
21 catalyst. The second phase is in sufficiently close proximity to the first phase to  
22 catalyze the oxygen scavenging reaction. When the oxygen scavenging material  
23 and the catalyst are in separate phases, processing difficulties, such as  
24 deactivation of the catalyst or shortened shelf-life, are avoided.

1 In another aspect of the invention, the catalyst is incorporated into a polymeric  
2 material to form at least one catalyst-containing layer. This layer is then brought  
3 into contact with the oxygen scavenging material. The particular polymeric  
4 material used is not critical as long as it does not deactivate the catalyst.

5 In another aspect of the invention, the oxygen scavenging composition or system  
6 can include a polymeric selective barrier layer. Such compositions are disclosed  
7 in U.S. Serial No. 08/304,303 filed September 12, 1994, the disclosure of which  
8 is incorporated herein by reference. The selective barrier layer functions as a  
9 selective barrier to certain oxidation by-products, but does allow the transmission  
10 of oxygen. Preferably, the layer prevents at least half of the number and/or  
11 amount of oxidation by-products having a boiling point of at least 40°C from  
12 passing through the polymeric selective barrier layer. Preferably, the selective  
13 barrier is located between the packaged item and the oxygen scavenging  
14 material.

15 The oxygen scavenging composition can also contain an oxygen barrier layer  
16 located on the outside of the scavenging layers to prevent the entry of oxygen  
17 into the sealed package. Typical oxygen barriers include poly(ethylene  
18 vinylalcohol), polyvinylalcohol, polyacrylonitrile, poly(vinyl chloride),  
19 poly(vinylidene dichloride), poly(ethylene terephthalate), silica coatings and  
20 polyamides such as Nylon 6, and Nylon 6,6 and MXD6. Copolymers of certain  
21 materials described above and metal foil layers can also be employed.

22 Additional layers such as adhesive layers or heat seal layers may also be  
23 employed. Adhesive layers include anhydride functionalized polyolefins.

1 The oxygen scavenging composition can include additives, stabilizers,  
2 plasticizers, fillers, pigments, dyestuffs, processing aids, anti-blocks, plasticizers,  
3 fire retardants, antifog agents, etc., which do not interfere with the oxygen  
4 scavenging function. The composition can also include antioxidants which inhibit  
5 the formation of free radicals and therefore improve storage of the oxygen  
6 scavenging composition prior to its use in oxygen scavenging applications. The  
7 presence of such antioxidants inhibits the initiation of the oxygen scavenging  
8 reaction until the photoinitiator is activated by radiation. Therefore, the amount  
9 employed will depend on the desired storage life of the composition, the  
10 photoinitiator, and the activation method employed.

11 The present oxygen scavenging compositions or systems are useful in improving  
12 the shelf-life of packaged oxygen-sensitive products such as food,  
13 pharmaceuticals, cosmetics, chemicals, electronic devices, and health and  
14 beauty products. The system can be used in rigid containers, flexible bags, or  
15 combinations of both. The system can also be used in moldings, coatings,  
16 strip/ribbon, patches, bottle cap inserts, and molded or thermoformed shapes,  
17 such as bottles and trays. In all of these applications, the oxygen scavenging  
18 composition effectively scavenges oxygen, whether it comes from the headspace  
19 of the packaging, is entrained in the food or product, or originates from outside  
20 the package.

21 Oxygen scavenging layers and articles are preferably prepared by melt-blending  
22 techniques. However, other methods such as the use of a solvent followed by  
23 evaporation may also be employed. When the blended composition is used to  
24 make film layers or articles, coextrusion, solvent casting, injection molding,  
25 stretch blow molding, orientation, thermoforming, extrusion coating, coating and

1 curing, lamination, extrusion lamination or combinations thereof would typically  
2 follow the blending.

3 The present invention will now be described further in terms of certain examples  
4 which are solely illustrative in nature and should in no way limit the scope of the  
5 present invention.

6 EXAMPLES

7 Example 1

8 Tribenzoyl Triphenylbenzene

9 The photoinitiator tribenzoyl triphenylbenzene was prepared by placing 300 mL  
10 nitrobenzene, 152 g (1.06 mole) benzoyl chloride, and 100 g (0.33 mole)  
11 triphenylbenzene into a 2 L 4-necked flask. The mixture was warmed to about  
12 60°C and 348 g (2.52 moles) aluminum trichloride was slowly added over a  
13 period of about 1 hour. The temperature rose to about 80°C and was maintained  
14 for about 4 hours. The mixture was cooled to about 40°C. The reaction mixture  
15 was poured into a solution of 340 g of HCl and 2 L water while stirring vigorously.  
16 The mixture was allowed to stand overnight and the water was decanted. The  
17 remaining mixture was filtered, washed with distilled water, and the wet cake was  
18 transferred into a 2 L 3-necked flask equipped with a mechanical stirrer. To the  
19 flask was added 900 mL distilled water. The reaction mixture was vacuum  
20 distilled until all nitrobenzene was removed. The reaction mixture was cooled,  
21 filtered and washed with water. The solid tribenzoyl triphenylbenzene was boiled  
22 in methanol, cooled and filtered. The solid was dissolved in 350 mL hot  
23 chloroform with activated carbon black and was boiled for 10 minutes and then  
24 filtered. The thus-prepared tribenzoyl triphenylbenzene solid was recrystallized

1 again with hot chloroform, washed with methanol, and dried. The product was  
2 characterized by NMR, UV, IR and exhibited a melting point of 195°C. The  
3 molecular weight determined by mass spectrometry was 618.

4 Benzoylated Styrene Oligomer

5 A mixture of styrene trimers was distilled from a polystyrene by-products stream.  
6 Then 95 g (0.3 mol) of this trimer mixture was slowly added to a solution of 218 g  
7 (2 moles) of benzoyl chloride and 134 g (1 mole) of  $\text{AlCl}_3$ . After stirring  
8 overnight, the mixture was poured into a solution of 250 g NaOH in 700 ml of  
9 water and 100 g of ice with constant stirring. Then 2000 ml of toluene was  
10 added to the mixture which was stirred an additional 2 hours. The mixture was  
11 filtered to remove  $\text{Al}(\text{OH})_3$  and the organic layer was washed twice with 500 ml  
12 portions of saturated NaCl solution followed by two additional washes with  
13 1000 ml of distilled water. The organic layer was dried overnight with  $\text{MgSO}_4$ .  
14 After filtering off the  $\text{MgSO}_4$ , the solvent was removed under vacuum on a rotary  
15 evaporator to yield 112 g of a dark brown, viscous liquid. Analysis of the product  
16 showed it comprised a mixture of mono-, di-, and tri-benzoylated compounds.  
17 The mixture comprises the non-extractable photoinitiators dibenzoylated  
18 1,1-diphenyl ethane, di-benzoylated 1,3 diphenyl propane, di-benzoylated  
19 1-phenyl naphthalene, dibenzoylated styrene dimer, and dibenzoylated styrene  
20 trimer.

21 Ditoluoyl Biphenyl

22 The photoinitiator ditoluoyl biphenyl was prepared by placing 300 mL  
23 nitrobenzene, 38.6 g (0.25 mole) biphenyl, and then 77.3 g (0.5 mole) p-toluoyl  
24 chloride into a 1 liter 4-necked flask equipped with a water condenser. The  
25 reaction mixture was cooled to -2°C. While stirring, 66.7 g (0.5 mole) aluminum

1 trichloride was added slowly over a period of about 20 minutes. During the  
2 reaction, the temperature increased to 14°C. The color changed from light  
3 yellow to reddish and then to dark green. The ice bath was removed and the  
4 reaction mixture was stirred at room temperature for 1 hour. The water bath  
5 temperature was increased to 67°C and stirred for 20 hours. The temperature  
6 was increased to about 90°C for 3 hours. The reaction mixture was poured with  
7 vigorous stirring into 1.2 L of 8% HCl solution. The mixture was stirred for  
8 1/2 hour, then 2 L chloroform was added. The organic layer was separated and  
9 washed with 2 x 1 L sodium bicarbonate solution followed by 2 x 1 L water. The  
10 organic layer was dried by magnesium sulfate. The solvent was removed by  
11 vacuum and the remaining solid was washed with 2 x 200 mL water. The  
12 thus-produced ditoluoyl biphenyl was dissolved in 1 L chloroform and 800 mL  
13 toluene and treated with carbon black. The mixture was heated for 10 minutes  
14 and filtered hot. The thus-produced ditoluoyl biphenyl crystallized out upon  
15 cooling and was dried under vacuum overnight.

16 Dibenzoyl Biphenyl

17 The photoinitiator dibenzoyl biphenyl was prepared by placing 200 mL  
18 nitrobenzene, 38.5 g (0.25 mole) biphenyl, and 140.6 g (1.00 mole) benzoyl  
19 chloride into a 1 liter 3-necked flask equipped with a water condenser. While  
20 stirring, 160 g (1.2 mole) aluminum trichloride was added slowly over a period of  
21 about 30 minutes. During the reaction, the temperature increased from 30°C to  
22 55°C. The color changed from yellowish to light brown, then reddish. The flask  
23 was kept in a water bath at a temperature of 55°C to 60°C for 3 hours while  
24 stirring. The reaction mixture was then cooled to 35°C. The reaction mixture  
25 was poured into 1.2 L of 8% HCl solution with vigorous stirring. The organic  
26 layer was separated and poured into a blender and 500 mL n-hexane was  
27 added. The mixture was vigorously stirred for 5 minutes and then filtered. The

1 solid was washed with n-hexane. The thus-produced dibenzoyl biphenyl was  
2 dried and recrystallized twice in chloroform.

3 Film Preparation

4 Oxidizable resin, carrier resin, catalyst and the photoinitiator to be evaluated  
5 were compounded in a twin screw extruder (Haake Rheocord TW-100 or Werner  
6 & Pfleiderer ZSK-30) at about 170°C. The carrier resin was polyethylene,  
7 PE1017, from Chevron and the oxidizable resin was styrene-butadiene-styrene  
8 copolymer, Vector 8508D from Dexco. The catalyst was 1000 ppm by weight  
9 cobalt in the form of cobalt oleate based on the total weight of the film. The  
10 indicated photoinitiator was present in the amount of 1000 ppm based on the  
11 total weight of the film. The compounded polymer containing the catalyst and  
12 40% Vector and 60% PE1017 was pelletized. A Randcastle cast film multi-layer  
13 micro extruder was employed to create three-layer films in an "ABA" structure in  
14 which "A", the outer layers, were 0.5 mil Dowlex 3010 polyethylene and "B", the  
15 inner layer, was 1.0 mil of the compounded polymer. Total film thickness was  
16 2.0 mils.

17 Head Space Oxygen Absorption

18 Samples of 5 x 20 cm size 3 layer films made above with an average weight of  
19 0.42 gram were irradiated under a 254 nm UV lamp for a fixed period of time  
20 (e.g., 1 minute, approximately 600 mJ/cm<sup>2</sup> of light energy measured at 254 nm).  
21 The film was immediately sealed in an aluminum foil bag which was evacuated  
22 and filled with 300 mL 1% oxygen. The oxygen content was monitored by  
23 Mocon oxygen headspace analyzer for a week and oxygen level recorded.

24 The results are graphically represented in Figures 1 and 2.

### Extraction Test

2 FDA recommendations for conducting migration (extraction) studies are found in  
3 "Recommendations for Chemistry Data for Indirect Food Additive Petitions",  
4 Food & Drug Administration (Chemistry Review Branch, Office of Premarket  
5 Approval, Center for Food Safety & Applied Nutrition), Washington, D.C. 20204,  
6 June 21, 1995.

7 Extraction tests were conducted using three methods. In the first extraction  
8 method, Method A, a 5 by 20 cm (15.5 sq. in.) piece of the film was irradiated (or  
9 not) and placed in a 20 ml headspace vial with 14 grams of ethanol. The vials  
10 were sealed with a crimped septum cap. The extraction period was 10 days at  
11 room temperature. The vials were opened and the film removed. The extracts  
12 were then stored at room temperature in the dark before testing.

In the second extraction method, Method B, a 2-inch diameter film sample was activated with 800 mJ/cm<sup>2</sup> UV, then placed in a gas tight cylindrical aluminum extraction cell. The extraction cell was flushed with gas containing 1% oxygen. A slight positive pressure was produced. Oxygen scavenging was allowed to occur within the cell at room temperature for 10 days. The oxygen scavenging results are graphically represented in Figures 1 and 2. Then 12.5 grams 95% ethanol was added to each cell through a septum. Residual volume of gas was set at 7-8 ml. The cell was inverted to allow contact of ethanol with the oxidized film and then placed in nitrogen cabinet at room temperature for 11 days. The extract was removed from the cells using a syringe needle in one septum and pressurizing the cell with nitrogen using a second needle in a second septum. The extracts were held in the dark at room temperature before testing.

- 1 In the third extraction method, Method C, film was extracted with Miglyol 812  
2 (derived from coconut oil) in an extraction cell as described in Method B at a ratio  
3 of 10 g solvent/in<sup>2</sup>. Samples were extracted at room temperature for 10 days.
- 4 The extracts from all methods were then analyzed for photoinitiator extractives  
5 using gas chromatography (GC-FID) or liquid chromatography (HPLC) methods  
6 which were calibrated using standard solutions of each photoinitiator. Those  
7 photoinitiators having low enough boiling points to permit them to pass through a  
8 GC column (DB-1, 0.5 mm ID, 60/5/10/300/60°C temperature program) were  
9 analyzed using gas chromatography. Anthrone, xanthone, 4-benzoyl biphenyl  
10 and dibenzoyl biphenyl were determined by gas chromatography. The remaining  
11 compounds could not be analyzed using gas chromatography methods because  
12 of their high boiling points. Liquid chromatography methods were used for these  
13 compounds.
- 14 In Table 1 below:
- 15 ANTH is anthrone.
- 16 XAN is xanthone.
- 17 BBP is 4-benzoyl biphenyl.
- 18 BBDE is 4,4'-bis(benzoyl)-diphenyl ether.
- 19 DBBP is dibenzoyl biphenyl.
- 20 BSO is benzoylated styrene oligomer comprising benzoylated styrene dimers,  
21 trimers and pentamers.
- 22 BBP<sup>3</sup> is tribenzoyl triphenylbenzene.

- 1 DTBP is ditoluoyl biphenyl.
- 2 Good oxygen scavenging compositions consumed half of the available oxygen in  
3 less than 4 days.
- 4 Fair oxygen scavenging compositions consumed half of the available oxygen in  
5 4-5 days.
- 6 Poor oxygen scavenging compositions consumed half of the available oxygen in  
7 greater than 6 days.
- 8 PI in extract is the amount of photoinitiator in ppb found in the extract  
9 (normalized to 10 g simulant/in<sup>2</sup> film).
- 10 DL is the detection limit defined as 3 times the instrument signal noise  
11 (normalized to 10 g simulant/in<sup>2</sup> film).

12

Table 1

Run	Photo-initiator	Days to reach 0.5% Oxygen	Extraction Method	Triggered UV-254	PI in Extract (ppb)	DL (ppb)
101	ANTH	NA*	A	No	663	7
102	ANTH	4-5	A	1 min.	63	7
103	ANTH	4-5	B	1 min.	85	26
201	XAN	NA	A	No	870	6
202	XAN	> 6	A	1 min.	269	6
203	XAN	> 6	B	1 min.	218	29
301	BBP	NA	A	No	834	6
302	BBP	3	A	1 min.	358	6
303	BBP	3	B	1 min.	357	26

Run	Photo-initiator	Days to reach 0.5% Oxygen	Extraction Method	Triggered UV-254	PI in Extract (ppb)	DL (ppb)
401	BBDE	NA	C	1 min.	1125	50
501	DBBP	3-4	A	1 min.	404	8
502	DBBP	3-4	B	1 min.	409	38
601	BSO	2-3	A	1 min.	ND**	30
602	BSO	2-3	B	1 min.	100	45
701	BBP <sup>3</sup>	2-3	A	1 min.	23	5
702	BBP <sup>3</sup>	2-3	B	1 min.	ND	20
801	DTBP	2-3	A	1 min.	ND	7
802	DTBP	2-3	B	1 min.	ND	30

1 \*Not Available

2 \*\*None detected

3 The Table above demonstrates the low leachability of and effective  
4 photoinitiation of the inventive photoinitiators. Runs 101-401 are submitted for  
5 comparative purposes. It is believed that removal of small molecular weight  
6 compounds from the BSO photoinitiator will further reduce its leachability.

7 Example 2

8 Three layer films were prepared as described in Example 1 with the exception of  
9 employing 1000 ppm by weight cobalt in the form of cobalt stearate as catalyst  
10 and benzoylated styrene oligomer and 4-benzoyl biphenyl individually as  
11 photoinitiators. The photoinitiators were also present at 1000 ppm by weight  
12 based on the oxygen scavenging composition.

1 The results are graphically represented in Figure 3. The results demonstrate the  
2 effectiveness of cobalt stearate and benzoylated styrene oligomer in providing  
3 good oxygen scavenging in a relatively short time.

4 Example 3

5 Benzoylated Meta-Terphenyl

6 Meta-terphenyl 115 gram (0.5 mole) and benzoyl chloride 232 grams (1.65 mole)  
7 were dissolved in 400 ml of nitrobenzene. The reactor temperature is  
8 maintained at 40-50°C while 440 grams of aluminum chloride (3.3 mole) was  
9 added in portions to control the exothermic reaction. The reaction mixture was  
10 increased to 80°C for 4 hours and then poured into 3 L of 5% HCl solution. The  
11 product was isolated by recrystallization from toluene and determined to be  
12 di-benzoylated meta-terphenyl. The melting point was 205-208°C. The UV  
13 spectra was similar to monomeric benzophenone. The molecular weight  
14 determined by mass spectrometer was 438 g/mole.

## 1 WHAT IS CLAIMED IS:

2 1. An oxygen scavenging composition comprising an oxygen scavenging  
3 material, a photoinitiator, and at least one catalyst effective in catalyzing  
4 oxygen scavenging,

5 wherein the photoinitiator comprises at least one benzophenone derivative  
6 containing at least two benzophenone moieties, and

7 wherein the photoinitiator is substantially non-extractable when the oxygen  
8 scavenging composition is exposed to a food simulant.

9 2. The oxygen scavenging composition according to Claim 1 wherein the  
10 photoinitiator is represented by the following formula:



12 wherein each X is a bridging group selected from the group consisting of  
13 sulfur; oxygen; carbonyl;  $-\text{SiR}_2-$ , wherein each R is individually an alkyl  
14 group containing from 1 to 12 carbon atoms, an aryl group containing 6 to  
15 12 carbon atoms, an alkoxy group containing from 1 to 12 carbon atoms;  
16  $-\text{NR}'-$ , wherein R' is an alkyl group containing 1 to 12 carbon atoms, an aryl  
17 group containing 6 to 12 carbon atoms, or hydrogen; and an organic group  
18 containing from 1 to 50 carbon atoms;

19 wherein m is 0 to 11;

20 wherein Y is a substituted or unsubstituted benzophenone group, wherein  
21 each substituent, R'', when present, is individually an alkyl, aryl, alkoxy,

- 1        phenoxy, or alicyclic group containing from 1 to 24 carbon atoms, or a  
2        halide; and
- 3        wherein n is 2-12.
- 4       3.    The oxygen scavenging composition according to Claim 2 wherein the  
5       combined molecular weight of X plus R" is at least 30 g/mole.
- 6       4.    The oxygen scavenging composition according to Claim 1 wherein less  
7       than 250 ppb of photoinitiator are extracted through a 0.5 mil polyethylene  
8       film at room temperature from an oxygen scavenging composition  
9       containing 1000 ppm by weight photoinitiator when exposed to 10 g fatty  
10      food simulant per square inch of 1 mil film at room temperature after  
11      10 days.
- 12      5.    The oxygen scavenging composition according to Claim 4 wherein less  
13      than 100 ppb of photoinitiator are extracted.
- 14      6.    The oxygen scavenging composition according to Claim 5 wherein less  
15      than 50 ppb of photoinitiator are extracted.
- 16      7.    An oxygen scavenging composition comprising an oxygen scavenging  
17      material, a photoinitiator, and at least one catalyst effective in catalyzing  
18      oxygen scavenging,
- 19      wherein the photoinitiator comprises at least one benzophenone derivative  
20      containing at least two benzophenone moieties, and

- 1        wherein the photoinitiator, after being irradiated with UV light, is  
2        substantially non-extractable when the oxygen scavenging composition is  
3        exposed to a food simulant, and
- 4        wherein the oxygen scavenging composition has an induction period of  
5        1 day or less.
- 6    8.    The oxygen scavenging composition according to Claim 7 wherein less  
7        than 250 ppb of photoinitiator are extracted from an oxygen scavenging  
8        composition containing 1000 ppm by weight photoinitiator when exposed to  
9        10 g fatty food simulant per square inch of 1 mil film at room temperature  
10       after 10 days.
- 11   9.    The oxygen scavenging composition according to Claim 8 wherein less  
12       than 100 ppb of photoinitiator are extracted.
- 13   10.   The oxygen scavenging composition according to Claim 9 wherein less  
14       than 50 ppb of photoinitiator are extracted.
- 15   11.   The oxygen scavenging composition according to Claim 8 which consumes  
16       half of the available oxygen in a container containing 1 percent oxygen in  
17       less than 4 days at 25°C.
- 18   12.   The oxygen scavenging composition according to Claim 11 which  
19       consumes half of the available oxygen in a container containing 1 percent  
20       oxygen in less than 4 days at 4°C.

- 1    13. The oxygen scavenging composition according to Claim 12 which exhibits  
2        an oxygen scavenging capability of at least 0.1 cc O<sub>2</sub>/gram of oxygen  
3        scavenging composition/day at 25°C.
- 4    14. The oxygen scavenging composition according to Claim 13 which exhibits  
5        an oxygen scavenging capability of at least about 0.5 cc O<sub>2</sub>/gram of oxygen  
6        scavenging composition/day at 25°C.
- 7    15. The oxygen scavenging composition according to Claim 14 which exhibits  
8        an oxygen scavenging capability of at least about 1 cc O<sub>2</sub>/gram of oxygen  
9        scavenging composition/day at 25°C.
- 10   16. The oxygen scavenging composition according to Claim 15 which exhibits  
11       an oxygen scavenging capability of at least about 1 cc O<sub>2</sub>/gram of oxygen  
12       scavenging composition/day at 4°C.
- 13   17. The oxygen scavenging composition of Claim 16 wherein the photoinitiator  
14       has a molecular weight in the range of about 360 to about 5000.
- 15   18. The oxygen scavenging composition of Claim 7 wherein the photoinitiator  
16       comprises tribenzoyl triphenylbenzene or substituted tribenzoyl  
17       triphenylbenzene, wherein the substituents are alkyl, aryl, alkoxy, phenoxy,  
18       or alicyclic groups containing from 1 to 24 carbon atoms or halides.
- 19   19. The oxygen scavenging composition of Claim 18 wherein the photoinitiator  
20       comprises tribenzoyl triphenylbenzene or tritoluoyl triphenylbenzene.
- 21   20. The oxygen scavenging composition of Claim 7 wherein the photoinitiator  
22       comprises benzoylated styrene oligomer or substituted benzoylated styrene

- 1        oligomer, wherein the substituents are alkyl, aryl, alkoxy, phenoxy, or  
2        alicyclic groups containing from 1 to 24 carbon atoms or halides.
- 3    21.   The oxygen scavenging composition of Claim 20 wherein the photoinitiator  
4        comprises di-benzoylated styrene trimer, tri-benzoylated styrene pentamer,  
5        tetra-benzoylated styrene pentamer or di-benzoylated styrene dimer.
- 6    22.   The oxygen scavenging composition of Claim 7 wherein the photoinitiator  
7        comprises substituted dibenzoyl biphenyl, wherein the substituents are  
8        alkyl, aryl, alkoxy, phenoxy, or alicyclic groups containing from 1 to  
9        24 carbon atoms or halides.
- 10   23.   The oxygen scavenging composition of Claim 22 wherein the photoinitiator  
11        comprises ditoluoyl biphenyl.
- 12   24.   The oxygen scavenging composition of Claim 7 wherein the photoinitiator  
13        comprises benzoylated terphenyl or substituted benzoylated terphenyl,  
14        wherein the substituents are alkyl, aryl, alkoxy, phenoxy, or alicyclic groups  
15        containing from 1 to 24 carbon atoms or halides.
- 16   25.   The oxygen scavenging composition of Claim 24 wherein the photoinitiator  
17        comprises dibenzoylated meta-terphenyl.
- 18   26.   The oxygen scavenging composition of Claim 7 wherein the photoinitiator is  
19        present in an amount in the range of from about 0.001 weight percent to  
20        about 10 weight percent based on the total weight of the oxygen  
21        scavenging composition.

- 1 27. The oxygen scavenging composition of Claim 26 wherein the photoinitiator  
2 is present in an amount in the range of from about 0.005 weight percent to  
3 about 5 weight percent based on the total weight of the oxygen scavenging  
4 composition.
- 5 28. The oxygen scavenging composition of Claim 7 wherein the oxygen  
6 scavenging material is an organic compound.
- 7 29. The oxygen scavenging composition of Claim 28 wherein the oxygen  
8 scavenging material is an ethylenically unsaturated organic compound.
- 9 30. The oxygen scavenging composition of Claim 28 wherein the oxygen  
10 scavenging material is an organic polymer.
- 11 31. The oxygen scavenging composition of Claim 30 wherein the oxygen  
12 scavenging material is polybutadiene, polyisoprene, styrene-butadiene  
13 block copolymers, acrylates which are prepared by transesterification of  
14 poly(ethylene-methyl acrylate), or a polyterpene.
- 15 32. The oxygen scavenging composition of Claim 31 wherein the oxygen  
16 scavenging material is poly(alpha-pinene), poly(dipentene),  
17 poly(beta-pinene), or poly(limonene).
- 18 33. The oxygen scavenging composition of Claim 31 wherein the oxygen  
19 scavenging material is styrene-butadiene-styrene block copolymer.
- 20 34. The oxygen scavenging composition of Claim 7 wherein the oxygen  
21 scavenging material is present in an amount in the range of from about

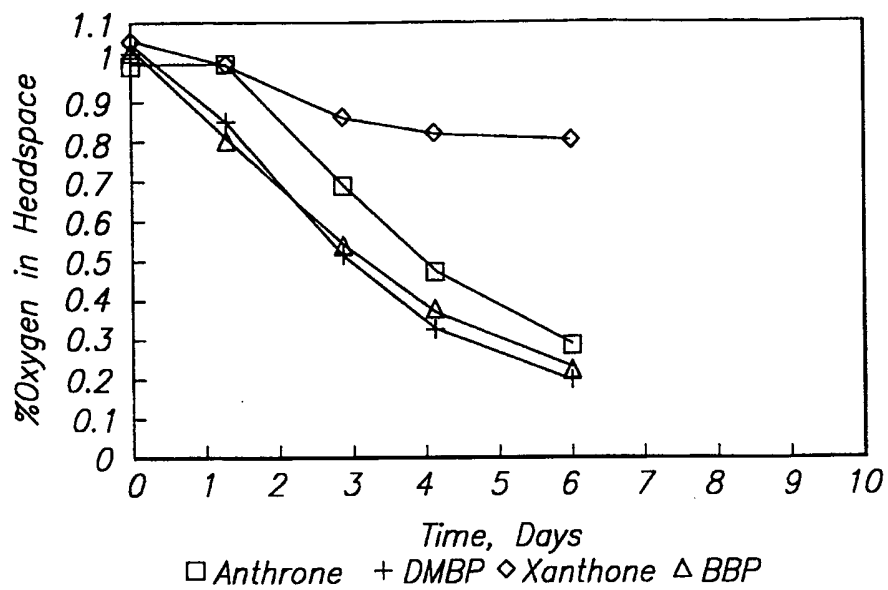
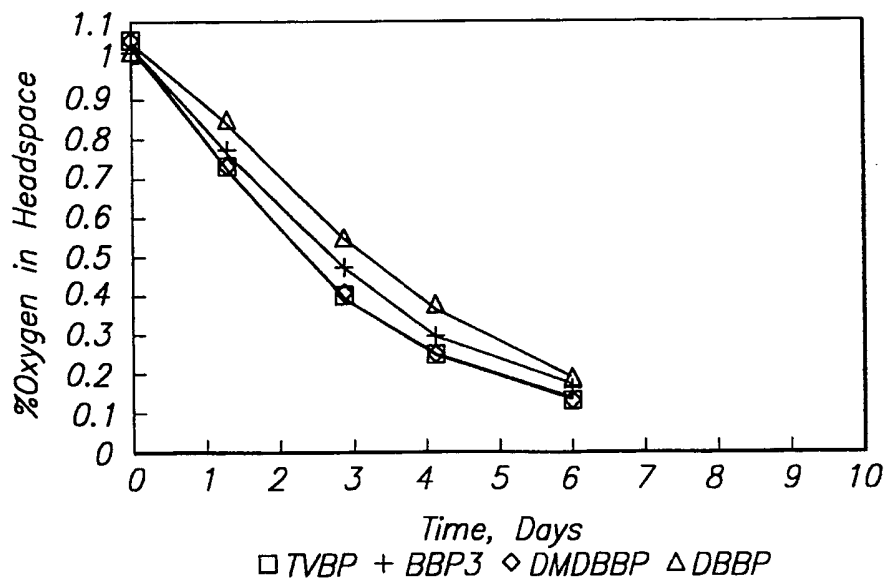
- 1        1 weight percent to about 99 weight percent based on the total oxygen  
2        scavenging composition.
- 3    35.   The oxygen scavenging composition of Claim 34 wherein the oxygen  
4        scavenging material is present in an amount in the range of from about  
5        5 weight percent to about 95 weight percent based on the total oxygen  
6        scavenging composition.
- 7    36.   The oxygen scavenging composition of Claim 35 wherein the oxygen  
8        scavenging material is present in an amount in the range of from 10 weight  
9        percent to 90 weight percent based on the total oxygen scavenging  
10       composition.
- 11   37.   The oxygen scavenging composition of Claim 7 wherein the catalyst is a  
12       transition metal salt.
- 13   38.   The oxygen scavenging composition according to Claim 37 wherein the  
14       catalyst is a cobalt salt.
- 15   39.   The oxygen scavenging composition according to Claim 38 wherein the  
16       catalyst is cobalt oleate, cobalt linoleate, cobalt neodecanoate, cobalt  
17       stearate, or cobalt caprylate.
- 18   40.   The oxygen scavenging composition according to Claim 39 wherein the  
19       catalyst is cobalt oleate.
- 20   41.   The oxygen scavenging composition according to Claim 39 wherein the  
21       catalyst is cobalt stearate and the photoinitiator is benzoylated styrene  
22       oligomer or benzoylated m-terphenyl.

- 1 42. The oxygen scavenging composition according to Claim 7 wherein the  
2 catalyst is present in an amount in the range of from about 10 ppm to about  
3 10,000 ppm transition metal ion based on the total weight of the oxygen  
4 scavenging composition.
- 5 43. The oxygen scavenging composition according to Claim 7 which is  
6 activated with radiation having a wave length in the range of from about  
7 200 to about 400 nm.
- 8 44. The oxygen scavenging composition according to Claim 7 wherein the  
9 oxygen scavenging material comprises a first phase and the catalyst  
10 comprises a second phase, wherein the second phase is in sufficiently  
11 close proximity to the first phase to catalyze an oxygen scavenging  
12 reaction.
- 13 45. The oxygen scavenging composition according to Claim 44 wherein the first  
14 phase forms a first layer and the second phase forms a second layer.
- 15 46. The oxygen scavenging composition according to Claim 45 wherein the  
16 second layer is in contact with the first layer.
- 17 47. The oxygen scavenging composition according to Claim 46 further  
18 comprising an oxygen barrier layer, a selective barrier layer, or a heat seal  
19 layer.
- 20 48. A film comprising the oxygen scavenging composition of Claim 7.
- 21 49. A film comprising the oxygen scavenging composition of Claim 45.

- 1     50. An article comprising the oxygen scavenging composition of Claim 7.
- 2     51. The article of Claim 50 wherein the article is a package.
- 3     52. The article of Claim 51 wherein the article is a package containing a food or  
4       beverage product, cosmetic, chemical, electronic device, pesticide or  
5       pharmaceutical.
- 6     53. The article of Claim 50 wherein the article is a patch, bottle cap insert, or  
7       molded or thermoformed shape.
- 8     54. The article of Claim 53 wherein the molded or thermoformed shape is a  
9       bottle or tray.
- 10    55. A method for scavenging oxygen within a package comprising sealing an  
11       oxygen-sensitive product in the package of Claim 47.
- 12    56. The method of Claim 55 wherein the package is activated with at least  
13       0.1 J/cm<sup>2</sup> UV radiation from 200 to 400 nm.
- 14    57. A method for preparing an oxygen scavenging composition comprising melt  
15       blending an oxygen scavenging material, a photoinitiator and at least one  
16       catalyst effective in catalyzing oxygen scavenging,
- 17       wherein the photoinitiator comprises a benzophenone derivative containing  
18       at least two benzophenone moieties, and
- 19       wherein the photoinitiator is substantially non-extractable when the oxygen  
20       scavenging composition is exposed to a food simulant.

- 1 58. A photoinitiator which is tribenzoyl triphenylbenzene or a substituted  
2 tribenzoyl triphenylbenzene, wherein the substituents are alkyl, aryl, alkoxy,  
3 phenoxy, or alicyclic groups containing from 1 to 24 carbon atoms or halides.
- 4 59. A method for preparing the photoinitiator of Claim 58 comprising reacting a  
5 substituted or unsubstituted benzoyl halide with a substituted or  
6 unsubstituted triphenylbenzene.
- 7 60. A photoinitiator which is benzoylated styrene oligomer or a substituted  
8 benzoylated styrene oligomer containing from 2 to 12 repeating styrenic  
9 groups, wherein the substituents are alkyl, aryl, alkoxy, phenoxy, or alicyclic  
10 groups containing from 1 to 24 carbon atoms or halides.
- 11 61. The photoinitiator according to Claim 60 wherein the benzoylated styrene  
12 oligomer comprises di-benzoylated styrene trimer, tri-benzoylated styrene  
13 pentamer, tetra-benzoylated styrene pentamer, and di-benzoylated styrene  
14 dimer.
- 15 62. A method for preparing the photoinitiator of Claim 61 comprising reacting  
16 substituted or unsubstituted styrene trimers with substituted or  
17 unsubstituted benzoyl halide.
- 18 63. A photoinitiator which is benzoylated meta-terphenyl or a substituted  
19 benzoylated meta-terphenyl.
- 20 64. A method for preparing the photoinitiator of Claim 63 comprising reacting  
21 meta-terphenyl or substituted meta-terphenyl with benzoyl halide or  
22 substituted benzoyl halide.

1/2

**FIG. 1****FIG. 2**

2/2

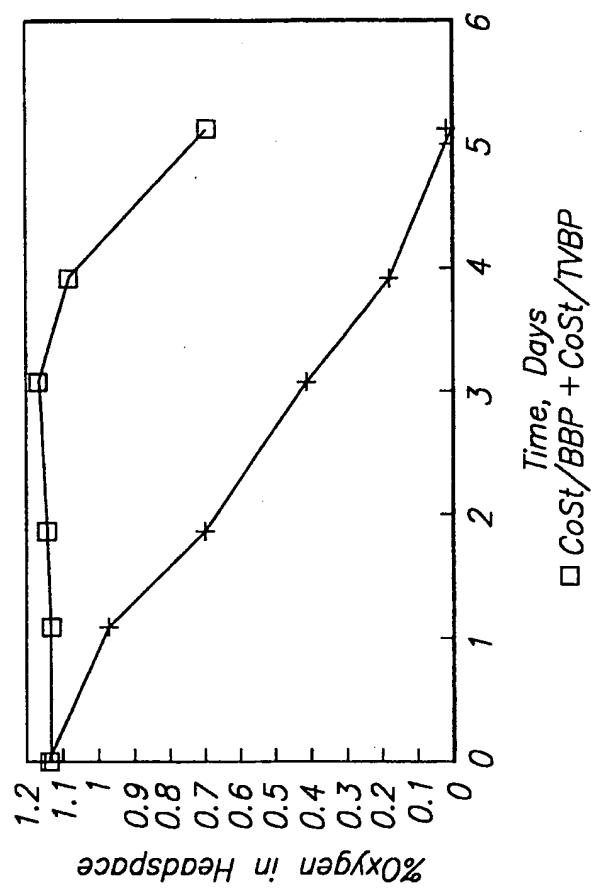


FIG. 3

# INTERNATIONAL SEARCH REPORT

Invention No.  
PCT/US 97/07734

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09K15/06 A23L3/3436 C07C49/786 C07C45/46 B32B27/18  
B65D81/26 B65D51/24 C08K5/00

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K A23L C07C B32B B65D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 211 875 A (SPEER DREW V ET AL) 18 May 1993 cited in the application see the whole document ---	1,7, 26-40, 42-57
Y	WO 96 33156 A (LAMBSON FINE CHEMICALS LIMITED ;ANDERSON DAVID GEORGE (GB); DAVIDS) 24 October 1996 see page 1, line 1 - page 3, line 10 compound C1, page 17 ---	1,7, 26-40, 42-57
A	WO 96 29362 A (GRACE W R & CO) 26 September 1996 see the whole document ---	1-57
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

**\* Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

15 July 1998

Date of mailing of the international search report

22/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

# INTERNATIONAL SEARCH REPORT

In International Application No.

PCT/US 98/07734

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 009, no. 119 (C-282), 23 May 1985 & JP 60 008303 A (ADEKA ARGUS KAGAKU KK), 17 January 1985, see abstract	63,64
A	---	1,7, 57-62
A	US 3 954 868 A (VON SCHMELING BOGISLAV ET AL) 4 May 1976 see column 8 - column 10 ---	58-64
A	US 3 663 712 A (SCHMELING BOGISLAV VON ET AL) 16 May 1972 see column 2, line 25 - line 35 ---	58-64
A	US 3 979 459 A (ROSE JOHN BREWSTER) 7 September 1976 see the whole document ---	58-64
A	US 4 672 079 A (LI BASSI GIUSEPPE ET AL) 9 June 1987 see column 5, line 37 - line 63 see column 6, line 45 - line 68 ---	60-62
P,A	EP 0 822 221 A (CLARIANT GMBH) 4 February 1998 see the whole document -----	1,7, 57-64

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 07734

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5211875 A	18-05-1993	AU 650140 B	09-06-1994
		AU 1811192 A	07-01-1993
		AU 659773 B	25-05-1995
		AU 5930594 A	16-06-1994
		CA 2071079 A	28-12-1992
		EP 0520257 A	30-12-1992
		FI 922969 A	28-12-1992
		HU 66841 A, B	30-01-1995
		IL 102160 A	27-11-1995
		JP 5194949 A	03-08-1993
		MX 9203389 A	01-12-1992
		PL 172392 B	30-09-1997
		SK 197192 A	07-09-1994
		RU 2093441 C	20-10-1997
		US 5425896 A	20-06-1995
		US 5498364 A	12-03-1996
WO 9633156 A	24-10-1996	EP 0822928 A	11-02-1998
WO 9629362 A	26-09-1996	AU 4869396 A	08-10-1996
US 3954868 A	04-05-1976	US 3808316 A	30-04-1974
		US 4044139 A	23-08-1977
		CA 975782 A	07-10-1975
		US 4202904 A	13-05-1980
US 3663712 A	16-05-1972	AT 304932 B	15-12-1972
		BE 756648 A	25-03-1971
		CA 942665 A	26-02-1974
		CH 529507 A	31-10-1972
		DE 2047370 A	01-04-1971
		FR 2063017 A	02-07-1971
		GB 1322075 A	04-07-1973
		JP 49001848 B	17-01-1974
		LU 61764 A	18-06-1971
		NL 7014195 A	29-03-1971
		ZA 7006461 A	27-05-1971
US 3979459 A	07-09-1976	GB 1420506 A	07-01-1976
		DE 2425199 A	12-12-1974

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In .tional .ation No

PCT/US 98/07734

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3979459 A		FR 2230615 A	20-12-1974
US 4672079 A	09-06-1987	BR 8501709 A	10-12-1985
		CA 1323463 A	19-10-1993
		EP 0161463 A	21-11-1985
		JP 1617436 C	12-09-1991
		JP 2036582 B	17-08-1990
		JP 60252443 A	13-12-1985
		JP 2160803 A	20-06-1990
		JP 7080927 B	30-08-1995
EP 0822221 A	04-02-1998	DE 19631244 A	12-02-1998
		AU 3236497 A	12-02-1998
		CZ 9702464 A	18-02-1998
		JP 10158243 A	16-06-1998
		NO 973555 A	03-02-1998

**THIS PAGE BLANK (USP10)**